

What is claimed is:

1. A resist composition, said composition comprising an acid-sensitive imaging polymer including a silsesquioxane backbone and a solubility inhibiting cyclic ketal pendant acid-labile moiety having a low activation energy for acid-catalyzed cleaving, and wherein at least a portion of said imaging polymer is fluorinated.

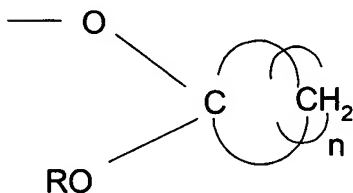
2. The resist composition of claim 1, further comprising a radiation-sensitive acid generator.

3. The resist composition of claim 1, wherein said imaging polymer further comprises a pendant solubility promoting moiety.

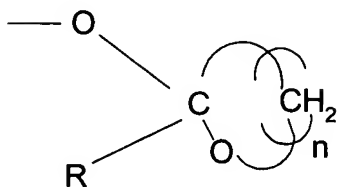
4. The resist composition of claim 3, wherein said pendant solubility promoting moiety is selected from the group consisting of a hydroxyl, a fluoroalcohol, a carboxylic acid, an amino group, an imino group, a fluorinated imino group and a fluorinated amino group.

5. The resist composition of claim 1, wherein at least a portion of said solubility inhibiting pendant cyclic ketal acid-labile moiety is fluorinated.

6. The resist composition of claim 1, wherein said cyclic ketal acid-labile moiety comprises a structure of the form



or



where n is any integer from 2 to 15 and R is an alkyl or a halogenated alkyl.

7. The resist composition of claim 1, wherein said cyclic ketal acid-labile moiety is selected from the group consisting of methoxycyclopropanyl, ethoxycyclopropanyl, butoxycyclohexanyl, methoxycyclobutanyl, ethoxycyclobutanyl, methoxycyclopentanyl, ethoxycyclopentanyl, methoxycyclohexanyl, ethoxycyclohexanyl, propoxycyclohexanyl, methoxycycloheptanyl, methoxycyclooctanyl, methoxynorbornyl and methoxyadamantyl.

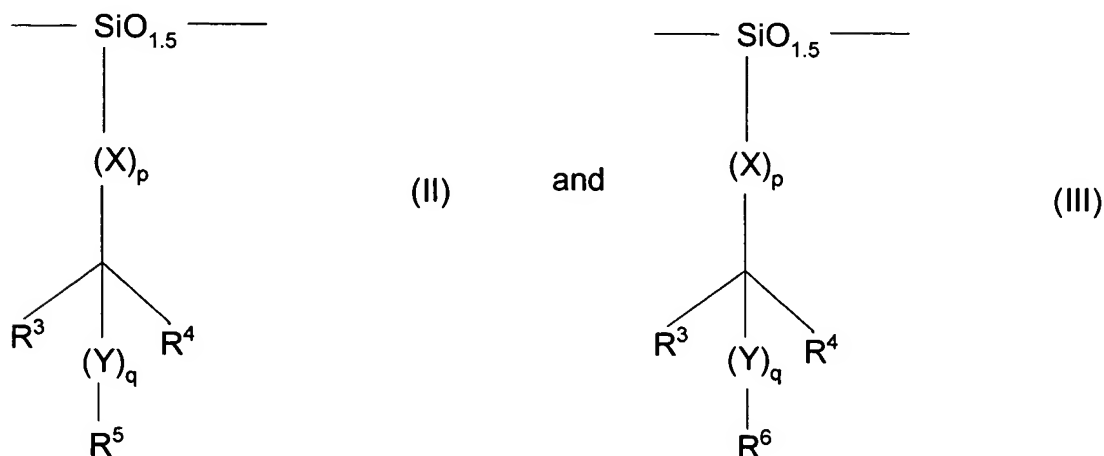
8. The resist composition of claim 1, wherein said cyclic ketal acid-labile moiety is substituted.

9. The resist composition of claim 1, wherein said cyclic ketal acid-labile moiety is substituted with fluorine or a hydrophobic moiety selected from the group consisting of —CF_3 , —CHF_2 , $\text{—CH}_2\text{F}$, —CCl_3 , —CHCl_2 and $\text{—CH}_2\text{Cl}$, and $\text{—Si(CH}_3)_3$.

10. The resist composition of claim 3, wherein at least a portion of said solubility promoting moiety is fluorinated.

11. The resist composition of claim 1, wherein said silsesquioxane polymer has a weight average molecular weight of about 800 to 500,000.

12. The resist composition of claim 1, wherein said imaging polymer comprises a combination of monomeric units (II) and (III) described by the formulas:



in which

each R^3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a linear alkyl, a branched alkyl, a cycloalkyl, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl, a halogenated aryl, or any combination thereof,

each X is independently selected from the group consisting of an oxygen atom, a sulfur atom, NR^3 , a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein p is an integer having the value 1 or 0,

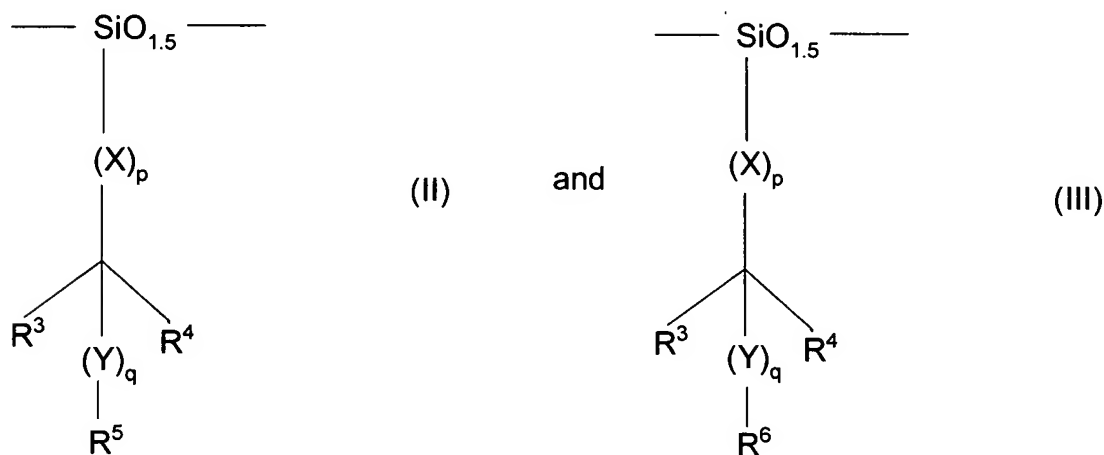
each Y is independently selected from the group consisting of a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein q is an integer having the value 1 or 0,

each R^4 is independently selected from the group consisting of a fluorine atom, a fluorinated linear alkyl, a fluorinated branched alkyl, a fluorocycloalkyl, a fluoroaryl, or any combination thereof,

each R^5 is independently a solubility inhibiting cyclic ketal group, and

each R^6 is independently a solubility promoting group.

13. The resist composition of claim 1, wherein said imaging polymer comprises a combination of monomeric units (II) and (IV) or units (II) and (V), wherein the monomeric units (II) and (III) are described by the formulas:



in which

each R^3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a linear alkyl, a branched alkyl, a cycloalkyl, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl, a halogenated aryl, or any combination thereof,

each X is independently selected from the group consisting of an oxygen atom, a sulfur atom, NR^3 , a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein p is an integer having the value 1 or 0,

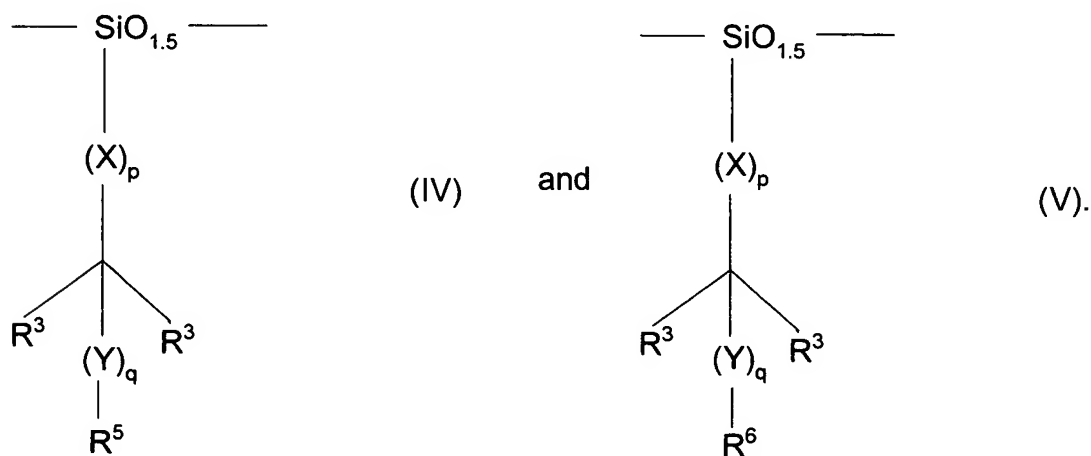
each Y is independently selected from the group consisting of a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein q is an integer having the value 1 or 0,

each R^4 is independently selected from the group consisting of a fluorine atom, a fluorinated linear alkyl, fluorinated branched alkyl, a fluorocycloalkyl, a fluoroaryl, or any combination thereof,

each R^5 is independently a solubility inhibiting cyclic ketal group, and

each R^6 is independently a solubility promoting group; and

the monomeric units (IV) and (V) are described by the formulas:



1 14. A method of forming a structure on a substrate, said method comprising the
2 steps of:

3 providing a substrate;

4 applying a resist composition to said substrate to form a resist layer on
5 said substrate, said resist composition comprising an acid-sensitive
6 imaging polymer comprising a silsesquioxane backbone, and a solubility
7 inhibiting pendant cyclic ketal acid-labile moiety having a low activation
8 energy for acid-catalyzed cleaving and wherein at least a portion of said
9 imaging polymer is fluorinated; and

10 patternwise exposing said substrate to radiation, whereby acid is
11 generated by said radiation-sensitive acid generator in exposed regions of
12 said resist layer;

13 removing patternwise soluble portions of said resist layer to form a pattern
14 of spaces in said resist layer; and

15 transferring said pattern of spaces to said substrate.
16

17 15. The method of claim 14 further comprising the step of baking the exposed
18 resist layer to promote acid-catalyzed reaction in exposed portions of said resist
19 layer.
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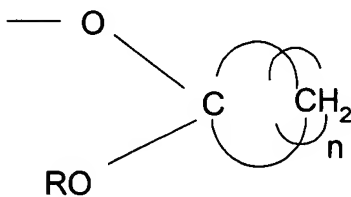
21 16. The method of claim 14 wherein said resist composition further comprises a
22 radiation-sensitive acid generator.
23

24 17. The method of claim 14, wherein said polymer further comprises a pendant
25 solubility promoting moiety.
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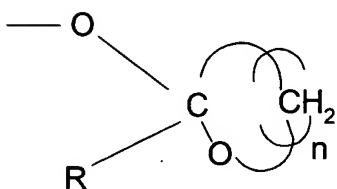
27 18. The method of claim 17, wherein said pendant solubility promoting moiety is
28 selected from the group consisting of a hydroxyl, a fluoroalcohol, a carboxylic
29 acid, an amino group, an imino group, a fluorinated imino group and a fluorinated
30 amino group.
31

1 19. The method of claim 14, wherein at least a portion of said solubility inhibiting
2 pendant cyclic ketal acid-labile moiety is fluorinated.

3
4 20. The method of claim 14, wherein said cyclic ketal acid-labile moiety
5 comprises a structure of the form
6



9 or



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13 where n is any integer from 2 to 15, and R is an alkyl or halogenated alkyl.

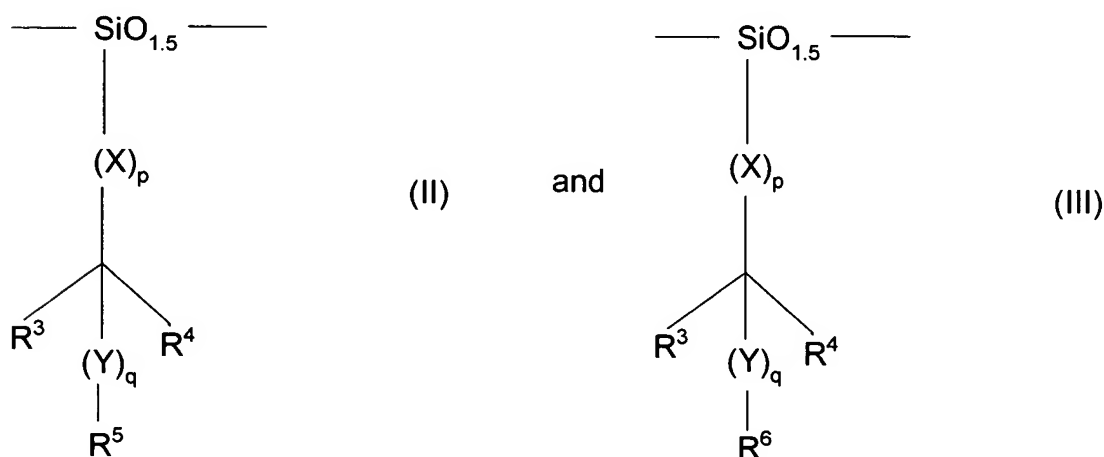
14
15 21. The method of claim 14, wherein said cyclic ketal acid-labile moiety is
16 selected from the group consisting of methoxycyclopropanyl,
17 ethoxycyclopropanyl, butoxycyclohexanyl, methoxycyclobutanyl,
18 ethoxycyclobutanyl, methoxycyclopentanyl, ethoxycyclopentanyl,
19 methoxycyclohexanyl, ethoxycyclohexanyl, propoxycyclohexanyl,
20 methoxycycloheptanyl, methoxycyclooctanyl, methoxynorbornyl and
21 methoxyadamantyl.

22
23 22. The method of claim 14, wherein said cyclic ketal acid-labile moiety is
24 substituted.
25

23. The method of claim 14, wherein said cyclic ketal acid-labile moiety is substituted with fluorine or a hydrophobic moiety selected from the group consisting of —CF_3 , —CHF_2 , $\text{—CH}_2\text{F}$, —CCl_3 , —CHCl_2 and $\text{—CH}_2\text{Cl}$, and $\text{—Si(CH}_3)_3$.

24. The method of claim 14, wherein said silsesquioxane polymer has a weight average molecular weight of about 800 to 500,000.

25. The method of claim 14, wherein said imaging polymer comprises a combination of monomeric units (II) and (III) described by the formulas:



in which

each R^3 is independently selected from the group consisting of a hydrogen atom, a halogen atom, a linear alkyl, a branched alkyl, a cycloalkyl, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl, a halogenated aryl, or any combination thereof,

each X is independently selected from the group consisting of an oxygen atom, a sulfur atom, NR^3 , a linear alkyl, a branched alkyl, a cycloalkyl, a halogenated

linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein p is an integer having the value 1 or 0,

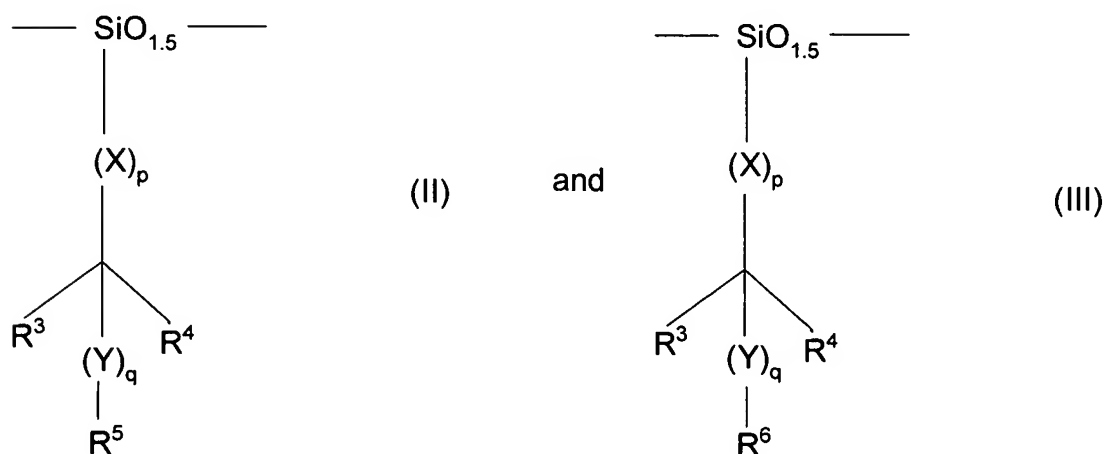
each Y is selected from the group consisting of a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein q is an integer having the value 1 or 0,

each R^4 is selected from the group consisting of a fluorine atom, a fluorinated linear alkyl, a fluorinated branched alkyl, a fluorocycloalkyl, a fluoroaryl, or any combination thereof,

each R^5 is independently a cyclic ketal solubility inhibiting group, and

each R^6 is independently a solubility promoting group.

26. The method of claim 14, wherein said imaging polymer comprises a combination of monomeric units (II) and (IV) or units (II) and (V), wherein the monomeric units (II) and (III) are described by the formulas:



1 in which

2
3 each R^3 is independently selected from the group consisting of a hydrogen atom,
4 a halogen atom, a linear alkyl, a branched alkyl, a cycloalkyl, a halogenated
5 linear alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl, a
6 halogenated aryl, or any combination thereof,

7
8 each X is selected from the group consisting of an oxygen atom, a sulfur atom,
9 NR^3 , a linear alkyl, a branched alkyl, a cycloalkyl group, a halogenated linear
10 alkyl, a halogenated branched alkyl, a halogenated cycloalkyl, an aryl group, or a
11 halogenated aryl, wherein p is an integer having the value 1 or 0,

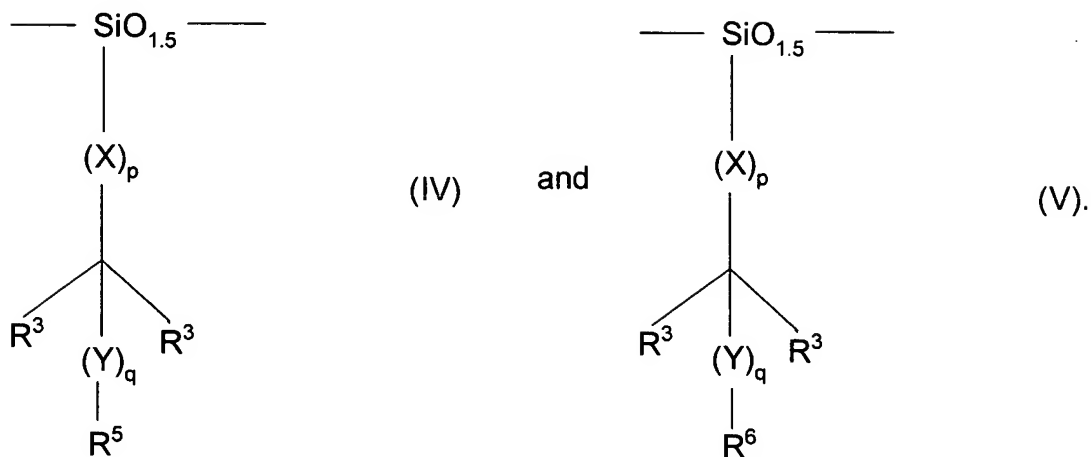
12
13 each Y is selected from the group consisting of a linear alkyl, a branched alkyl, a
14 cycloalkyl group, a halogenated linear alkyl, a halogenated branched alkyl, a
15 halogenated cycloalkyl, an aryl group, or a halogenated aryl, wherein q is an
16 integer having the value 1 or 0,

17
18 each R^4 is independently selected from the group consisting of a fluorine atom, a
19 fluorinated linear alkyl, a fluorinated branched alkyl, a fluorocycloalkyl, a
20 fluoroaryl, or any combination thereof,

21
22 each R^5 is independently a cyclic ketal solubility inhibiting group, and

23
24 each R^6 is independently a solubility promoting group; and

25
26 the monomeric units (IV) and (V) are described by the formulas:
27



27. The method of claim 14, further comprising forming a planarizing layer over said substrate, wherein said resist layer is applied directly to said planarizing layer, and etching said planarizing layer through said pattern of spaces in said resist layer to expose said substrate.

28. The method of claim 27, wherein said planarizing layer has an underlayer composition comprising:

(A) a polymer containing (i) cyclic ether moieties, (ii) saturated polycyclic moieties, and (iii) aromatic moieties if said underlayer composition does not require a separate crosslinker, or

(B) a polymer containing (i) saturated polycyclic moieties, and (ii) aromatic moieties if said underlayer composition requires a separate crosslinker.

29. The method of claim 28, wherein said underlayer composition further comprises a fluorinated polycyclic moiety, a fluorinated aromatic moiety or a combination thereof.

30. The method of claim 14, wherein said step of transferring further comprises a method selected from the group consisting of depositing, implanting, plating and etching.